

## **APPENDIX C**

### **CHARACTERIZATION OF ORE, WASTE ROCK, AND TAILINGS**

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## 1.0 GOALS AND PURPOSE OF THE APPENDIX

EPA expects that applicants will conduct a sufficient number and variety of environmental tests on a representative suite of samples in order to support projections of wastewater and solid waste management practices and effluent quality. This appendix describes the methods used to characterize the solid wastes from mining activities and the rationale for their implementation. The materials in this appendix complement those in Appendix B, *Receiving Waters* and Appendix F, *Solid Waste Management*.

Determining the physical and chemical character of solid waste materials is a prerequisite to delineating the area that would be affected by waste disposal; recognizing the physical, chemical, and biological impacts of waste disposal; and developing appropriate mitigation measures. Environmental test samples should be collected as part of a comprehensive program designed to examine the range of conditions that occur or could occur. For areas in which mining has concluded or is on-going, tested materials should be produced by normal mine operations. For areas in which mining is proposed or production methods are expected to change, tested materials should include batch and pilot-plant waste products. Physical and chemical characterization studies should be conducted in a manner that provides conservative estimates of the potential environmental impacts.

An environmental sampling program should be related to the mine plan and should be designed to represent the different lithologic units that have been or will be encountered, excavated, processed, disposed of, or exposed (for example in pit walls). It should establish the chemical and physical variability of each geologic unit encountered at the mine site, including borrow materials. It can have the benefit of reducing or eliminating the potential future costs associated with mismanagement of disposed materials. For proposed or expanding mining activities, ore sample testing should be representative of the range of materials that will be mined and wastes that will be generated. Although simple in concept, developing and implementing a reliable environmental sampling program may be a complex endeavor.

This appendix presents the methods used to determine the physical and chemical characteristics of waste materials, describes the environmental tests used to assess contaminant mobility, outlines the conceptual models used to analyze contaminant fate and transport, and discusses the elements of quality assurance and quality control engendered in an environmental testing program.

## 2.0 ANALYSIS OF PHYSICAL CHARACTERISTICS

### 2.1 Extent of Analysis

The proposed mine plan should be used to determine the types and volumes of materials that will be excavated or otherwise disturbed and the management of those materials. This information, some of which can be presented in the form of maps and cross-sections, provides the basis for determining the types of characterization studies that will be needed. For example, if waste rock materials will be used in road construction, then the potential effects on water

quality will need to be ascertained. If the gangue rock at the site consists of several lithologic types that will be mined in sequence, then the resulting waste rock dump could contain vertical or lateral changes in rock type that might impact water quality models and geotechnical stability. Because many material or waste dumps cover significant areas, characterization studies of substrate materials can determine whether lateral changes in physical properties are present that could impact dump stabilities and contaminant transport models. Although the physical and chemical characterization of solid materials can be an intricate process, a well-planned and executed program can provide the benefits of improved project design and environmental impact mitigation.

## 2.2 Physical Parameters

The physical characteristics of waste materials govern their hydrologic properties and physical stability. Important parameters that affect porosity and permeability include particle size, particle-size distribution, particle-size grading, stratification, and mineral composition. Important parameters that affect stability include stratification, mineral composition, cohesion, compaction, moisture retention, shrink-swell potential, Atterberg limits, and bulk density. For existing waste rock dumps and tailings piles, physical characteristics testing should determine whether the disposed material contains vertical or lateral changes in physical properties sufficient to affect the flow of leachate or the stability of the pile. Such variations could arise from changes in mining, processing, and disposal methods; variations in the geology of the ore or gangue materials as mining progressed; or the effects of subaerial weathering, alteration, and secondary mineral growth after the materials were emplaced.

*Particle-size characteristics* (median diameter, sorting, size distribution) are determined through mechanical analyses (sieve analysis). Those of fine-grained materials (smaller than 50 microns) are determined using methods based on particle settling velocities (e.g., pipette analysis) or optical techniques (e.g., Coulter counters). The American Society for Testing and Materials provides methods for determining particle-size characteristics (ASTM, 1996); additional methodologies can be found in Sobek et al. (1978).

*Particle-size grading* (i.e., changes in particle size normal to a bedding surface) typifies many waste rock dumps constructed by end-dumping. Grain-dispersive forces that occur as materials avalanche down the working face of a waste rock dump can create deposits that become coarser upward and outward (e.g., Blatt et al., 1980). Changes in particle-size grading potentially can form preferred pathways for the flow of water through waste rock piles.

*Stratification* can be created within waste rock and spent ore dumps and tailings piles by construction practices. In addition to affecting fluid flow, bedding surfaces can serve as planes of weakness along which slope failure can occur. The presence of stratification can be noted from visual observation of existing waste materials or drill cores obtained from these materials.

Methods to measure *cohesion*, *compaction*, *moisture retention*, *shrink-swell potential*, *Atterberg limits*, and *bulk density* have been developed by the American Society for Testing and Materials (ASTM, 1996). These parameters are particularly important for assessing the stability of waste rock and spent ore dumps, tailings piles, and pit benches. For existing waste materials,

vertical or lateral changes in the amount and type of clay minerals can cause many of these parameters to change throughout a deposit. Consequently, existing waste deposits should be sampled in several locations and at several depths to determine the range of values that occur. For those tests that cannot be conducted on materials *in situ*, appropriate ASTM procedures should be followed to ensure sample integrity. The stability of waste rock dumps and tailings piles is discussed in more detail in Appendix F.

## 2.3 Mineralogical Composition

Mineralogical composition and mineral textures can be determined using a petrographic (polarizing light) microscope equipped with both transmitted and reflected light. Samples can be viewed in thin-section, as grain mounts, or as discrete grains. Mineral percentages can be estimated through counts of a statistically significant number of points or grains. Thin-sections are particularly useful for recognizing mineral reaction (alteration) textures and products that may influence the interpretation of geochemical test results as described in the next section. Moreover, they permit identification of reaction products that may form as a consequence of mineral processing (by examining samples “before” and “after” processing). Petrographic techniques, including oil immersion, are well-established and widely accepted (Kerr, 1977; Sobek et al., 1978; Gribble and Hall, 1993; Craig and Vaughn, 1994).

X-ray diffraction (XRD) is used to identify minerals that are difficult to resolve with a petrographic microscope and to characterize crystal structures. The method measures the diffraction of an incident beam of X-rays during its passage through a crystal structure caused by atoms or atomic layers in the crystal (e.g., Hutchison, 1974; Bish and Post, 1989). The technique is a quick and easy means to determine the compositions of clay minerals that are associated with many ore deposits (e.g., Sobek et al., 1978). Analyzing clay minerals, which have different sorptive properties, can provide useful data that can be used in the design of waste rock and tailings piles, drainage covers, compacted liners, and remediation plans.

Scanning electron microscopy (SEM) can be used to image reaction products and grain coatings that cannot be resolved with an optical (petrographic) microscope. For example, it can be used to gather data on secondary mineral growths in the pore spaces of waste materials. This knowledge can be used to refine models of fate and transport by clarifying the potential for contaminant sorption onto the surfaces of clays or other minerals. In addition, the technique can be used to gather quantitative or semi-quantitative chemical data on the major constituents of minerals at scales that vary from a few microns to a few millimeters. The SEM scans a tightly focused beam of high-energy electrons across the surface of a prepared sample. The beam dislodges secondary electrons from the atoms in the sample, which are then collected, counted and formed into an image of the specimen surface (e.g., Goldstein et al., 1981). Because the energies with which secondary electrons are emitted are unique to each element, secondary electrons also provide compositional data through energy dispersive microanalysis.

Electron microprobe (EMP) analysis is used to determine the compositions of mineral grains in a sample. The EMP focuses a beam of high-energy electrons onto a fixed spot on a sample surface (typically 1 to 2 microns in diameter). The beam dislodges secondary electrons that emit radiation in wavelengths and energies characteristic of particular elements. Similar to

SEM analysis, EMPs can be operated in an energy dispersive analysis mode. However, these machines typically are operated using wavelength dispersive detectors, which provide lower detection limits and more accurate analyses. Because it utilizes a tightly focused incident beam of high energy, EMP microanalysis is poorly suited for determinations of light elements (atomic number less than 10) and volatile elements.

### 3.0 ANALYSIS OF CHEMICAL COMPOSITION

Acceptable techniques for determining the concentrations of inorganic and organic constituents in solid and liquid wastes are given in 40 CFR, Part 136.3. Analytical methods are detailed in publications by the U.S. EPA (1983; 1986a), American Public Health Association (APHA et al., 1992), American Society for Testing and Materials (ASTM, 1996), and the U.S. Geological Survey (Fishman and Friedman, 1989). Considerations regarding the number and types of samples that should be tested are described in Section 6.0.

#### 3.1 Analysis of Solids

The chemical composition of solid materials such as waste rock, tailings, or spent ore can be determined using a variety of techniques. Most analytical techniques require solubilization of the solid material into a liquid form prior to analysis. An exception is *X-ray fluorescence (XRF)*, which is a common technique used to determine the major and minor chemical constituents of rocks and minerals (Norrish and Chappell, 1967; Bertin, 1970; Johnson and Maxwell, 1981). The technique analyzes sample materials in solid form (either as compacted powders or powders that have been fused into glass) by bombarding the sample with X-rays of known wavelength and energy. Excitation by the primary X-rays induces emissions of secondary photons (fluorescence) with energies and wavelengths characteristic of individual elements. The number of photons emitted (intensity) at a given wavelength or energy is proportional to the abundance of a given element. X-ray fluorescence is capable of determining the abundance of many elements that occur in concentrations of a few parts per million. It is an inferior technique for light elements, volatile elements, and many elements occurring at concentrations of less than 10 ppm.

Solid samples commonly are solubilized using strong-acid dissolution. Methods to digest solid materials in nitric acid are common and widely accepted (ASTM D5198 [ASTM, 1996]; EPA Method 3051 [U.S. EPA, 1986a]). The subsequent liquids can be analyzed by several methods that most commonly include atomic absorption spectrometry, inductively coupled plasma spectrometry, and colorimetry.

In *atomic absorption (AA) spectrometry*, samples are vaporized at high temperatures and the concentrations of selected elements are determined by measuring the absorption of light at wavelengths characteristic of that element (Harris, 1987; Patniak, 1997). The technique is highly sensitive, comparatively simple, and permits determination of a variety of metals to levels of parts per million or less. In the direct aspiration method, sample solutions are injected into a flame, where they are dissociated and made amenable to absorption. The more sensitive graphite furnace technique uses an electrically heated furnace to vaporize the sample solution. The graphite furnace technique affords lower detection limits, but is more sensitive to matrix

interference effects; it works best on relatively “clean” samples (U.S. EPA, 1986a). A primary disadvantage of the AA technique is that it is time-consuming, because each element must be analyzed separately (i.e., a sample must be analyzed repeatedly). Accepted atomic absorption techniques using both methods are given in U.S. EPA (1983; EPA 200 series methods) and U.S. EPA (1986a; EPA 7000 series). Methods for determining trace metal concentrations at levels of a few tens to hundreds of parts per trillion were recently developed by U.S. EPA (1996d, f). The absorption of elements that occur at low concentrations can be masked by interference from elements at higher concentrations. Consequently, chemical separation is used to isolate these elements and permit their analysis without interference. The cold-vapor technique (EPA Methods 245.1 and 245.2, U.S. EPA [1983]; EPA Method 7470A, U.S. EPA [1986a]; EPA Method 1631 for low detection limits, U.S. EPA [1996a]) is used to reduce and isolate mercury for analysis. The gas hydride method is used to reduce and isolate selenium (EPA Method 7741A; U.S. EPA [1986a]) and arsenic (EPA Method 7061A; U.S. EPA [1986a]; EPA Method 1632 for low detection levels; U.S. EPA [1996b]) for analysis. A co-precipitation method (EPA Method 218.5, U.S. EPA [1983]; EPA Method 7195, U.S. EPA [1986a]) is used to remove trivalent chromium from solution, permitting measurement of hexavalent chromium in the remaining solution by AA.

In *inductively coupled plasma (ICP) spectrometry*, aqueous samples are ionized at extreme temperatures in an argon plasma. The ions are focused into a stream of material that is accelerated toward detectors that measure either the photon emissions at specific wavelengths (ICP-AES, atomic emission spectrometry) or the masses of specific isotopes (ICP-MS, mass spectrometry) (Robinson, 1990). Standard ICP techniques can detect elements in concentrations of a few parts per billion to parts per million, but recently developed guidelines permit detection of a few to a few hundred parts per trillion. The primary advantage of ICP analysis is that it permits rapid, simultaneous or sequential determination of multiple elements in a single analytical session (i.e., a sample need only be analyzed once). Disadvantages include interference from the plasma gases, background radiation from other elements, and interferences from large excesses of single elements (U.S. EPA, 1986a). Accepted standard ICP techniques using both methods are given in U.S. EPA (1986a; EPA Method 6010A for ICP-AES; EPA Method 6020 for ICP-MS). “Ultraclean” ICP-MS techniques that permit low detection limits are given in U.S. EPA (1996e, 1996g).

*Colorimetry* is a type of spectrophotometric analysis that uses the absorption of visible radiation (Harris, 1987; Patniak, 1997) to determine concentration. The technique uses a spectrophotometer or filter photometer to determine the concentration of a constituent in a specially prepared aqueous solution by measuring the absorbance at a specific visible light wavelength. An accepted colorimetric technique for hexavalent chromium (EPA Method 7196A) is given in U.S. EPA (1986a). Colorimetric techniques also have been developed for nitrate-nitrogen, nitrate plus nitrite-nitrogen, ammonium nitrogen, and total cyanide.

### 3.2 Analysis of Liquids

Samples of waters and wastewaters typically are filtered in the field prior to analysis. Methods developed by EPA require filtration using a 0.45 µm filter. Care should be taken when



reusing field filters to ensure that they do not become sources of contamination. Importantly, some colloidal particulates can pass through this filter and will report as dissolved constituents in water quality analyses. Because some of these constituents (e.g., iron oxyhydroxides) readily adsorb metals from solution, the presence of colloidal particles smaller than 0.45  $\mu\text{m}$  can influence measurements of dissolved metals such as cadmium, copper, lead, and zinc.

Liquid samples may be analyzed as collected, but they typically are treated following collection to preserve their chemical constituents. In many cases, multiple splits of a given sample are preserved using a variety of techniques. Electrical conductivity and pH should be measured on untreated samples at the time of collection. In contrast, samples that must be delivered to a lab for analysis of their inorganic and organic constituents are preserved to preclude precipitation of metal compounds or the volatilization of organic compounds between the time of sample collection and analysis. Samples collected for total metals analysis should be acidified to pH <2.0 using nitric acid and stored at 4EC to permit dissolution of suspended constituents (EPA Method 200.0; U.S. EPA [1983]). In contrast, samples collected for cyanide analysis should be adjusted to pH >12.0 using sodium hydroxide and stored at 4EC to prevent the formation of hydrogen cyanide (EPA Method 335.3; U.S. EPA [1983]). Samples collected for analysis of their organic constituents should be preserved at 4EC and left untreated or treated with sodium thiosulfate (EPA 3500 and 5000 series methods; U.S. EPA [1986a]).

Many metals in ambient waters occur in concentrations of less than 1 part per billion, which are below the detection limits of most standard analytical techniques. To permit accurate determinations of background water quality, the U.S. EPA recently released draft Method 1669 (U.S. EPA, 1996h). This method provides guidance for collecting samples that will be analyzed by newly developed “ultraclean” ICP-MS, AA, and ion chromatographic techniques (U.S. EPA, 1996a-g). Using these sampling and analytical methods, trace metal constituents in ambient water can be determined at levels of a few to a few hundred parts per trillion.

Prior to analysis, organic constituents are separated using solvent extraction or purge-and-trap techniques. Nonvolatile and semi-volatile organic compounds are extracted using solvents such as methylene chloride and techniques that include liquid-liquid extraction, soxhlet extraction, or ultrasonic extraction (EPA 3500 series methods; U.S. EPA [1986a]). Volatile organic compounds are extracted by bubbling an inert gas (either  $\text{N}_2$  or He) through the sample solution to liberate the volatile components which are trapped in a sorbent column (EPA 5000 series methods; U.S. EPA [1986a]).

The concentrations of metals and other inorganic cationic constituents in samples of surface water, ground water, waste rock leachate, or mine drainage are analyzed using the AA, ICP, and colorimetric methods described above. Other techniques used to analyze aqueous samples include titrimetry, gravimetry, ion-selective electrode analysis, ion chromatography, gas chromatography, liquid chromatography, and Fourier transform infrared spectroscopy.

*Titrimetric* analysis is used to measure the acidity and alkalinity of aqueous samples (Patniak, 1997). Acidity is measured by titrating a solution to a predetermined pH endpoint using sodium hydroxide (EPA Method 305.2; U.S. EPA [1983]). Alkalinity is determined by titrating a solution to a predetermined pH endpoint using a strong acid (EPA Method 310.1; U.S.

EPA [1983]). In both cases, the amount of titrant is converted to milliequivalents of acidity or alkalinity per liter of solution.

In *gravimetric analysis*, the mass of a reaction product is used to determine the quantity of the original analyte (Harris, 1987). Although these techniques are among the most accurate in analytical chemistry, they are no longer widely used because they are time consuming. However, gravimetric analysis remains the most common method for determining total dissolved solids (TDS) and total suspended solids (TSS) in a sample. To determine these parameters, a sample is filtered through a standard glass fiber filter. The filter is dried and weighed, with the weight increase representing TSS concentration (EPA Method, 160.2; U.S. EPA [1983]). Total dissolved solids are measured by evaporating the filtrate and weighing the residual solids (EPA Method 160.1; U.S. EPA [1983]).

*Ion-selective electrodes* respond to a single ionic species in solution (Harris, 1987; Patniak, 1997). The electrodes measure the electrical potential difference across a membrane between a solute at constant chemical activity within the electrode and the activity of the solute in the solution of interest. Ion-selective electrodes can be used to measure the concentrations of fluorine, cyanide, and ammonia in water samples (Standard Method 4500 series; APHA et al. [1992]).

*Chromatographic techniques*, in which constituents of interest are separated from one another to permit their identification, include ion chromatography, gas chromatography, and high-performance liquid chromatography. *Ion chromatography* is used to measure the concentrations of common anionic constituents (EPA Method 300.0; U.S. EPA [1983]). The technique uses a series of columns filled with ion-exchange resins to separate the anions from solution and combine them with hydrogen to form acids (Harris, 1987; Patniak, 1997). The electrical conductivities of the different acids, which are variably strong electrolytes, are measured using a conductivity detector, from which anion concentrations can be determined. A method for determining low levels of hexavalent chromium by ion chromatography was recently developed by U.S. EPA (1996c). *Gas chromatography* is used to measure the concentrations of a wide variety of organic constituents. In this technique, a liquid sample is vaporized and carried by an inert gas through a column filled with a partitioning material (Harris, 1987; Patniak, 1997). Organic compounds are separated in the column by their variable affinities for the partitioning material, which causes the different compounds have discrete retention times prior to emerging from the column and flowing to a detector. Several detector types are employed including electrolytic conductivity detectors, electron capture detectors, and flame ionization detectors (EPA 8000 series methods; U.S. EPA [1986a]). More sensitive detection can be accomplished by using mass spectrometers (EPA 8200 series methods; U.S. EPA [1986a]). Constituents that cannot be differentiated by mass (i.e., isomers) can be distinguished using *Fourier transform infrared spectroscopy*, in which isomers are distinguished by their infrared absorption frequencies (EPA Method 8410; U.S. EPA [1986a]). *High-performance liquid chromatography* also is used to measure the concentrations of organic constituents. This technique uses columns filled with adsorbent material (typically microporous silica with a covalently bonded stationary phase) to separate the compounds of interest, which are then eluted from the column by solvents (Harris, 1987; Patniak, 1997; EPA 8300 series methods, U.S. EPA [1986a]). Liquid flow is accomplished under high pressure to increase efficiency of the system. Absorbance, refractive

index, and polarographic monitors are used to detect solutes eluted from the column. Potential interferences occur in all chromatographic techniques when two or more solutes have similar retention times in the separation column or, for mass spectrometry, have similar masses.

## 4.0 ANALYSIS OF CONTAMINANT MOBILITY FROM SOLIDS

Rigorous geochemical testing programs can reveal whether the rocks exposed by the mining process or the wastes and materials produced by extractive operations are likely to release metals or other contaminants that could degrade the environment at or surrounding a mine site. Testing programs are aimed at determining the potential for acid generation and constituent release through weathering and leaching. Because these laboratory programs are conducted in a manner intended to speed natural processes, test results must be interpreted with caution. Particle size and mineralogy play pivotal roles that govern the long-term behavior of materials in the environment. Consequently, these variables should not be ignored by a testing program. Considerations regarding the number and types of samples that should be tested are described in Section 6.0.

### 4.1 Mineralogical Considerations

It is critical to understand the mineralogy of waste rock, tailings, and spent ore materials in order to establish a sound geochemical testing program. Because many ore deposits and their gangue materials are chemically and mineralogically zoned (also true of some waste rock dumps and tailings piles), selecting appropriate test materials requires knowledge of mineral composition, abundance and distribution. Recognizing spatial variations in mineral abundance is especially important for potentially reactive sulfides (e.g., pyrite), nonreactive but leachable sulfides (e.g., galena), acid- and nonacid-sulfates (e.g., jarosite and gypsum), readily soluble and comparatively insoluble carbonates (e.g., calcite and siderite), and other minerals that may affect test results (e.g., clays and feldspars). Smith et al. (1994) showed that alteration zoning can have a significant impact on the pH and metals content of drainage generated from a quartz-alunite epithermal deposit. Testing programs need to recognize the mineralogical changes that secondary alteration may have imparted to a given rock unit and characterize the range of environmental behavior that could occur as a result.

Mineralogical studies provide a framework for interpreting the results of the geochemical tests outlined below. For example, hydroxide coatings on calcite or sulfate coatings on pyrite may preclude these minerals from participating in acid neutralization or generation in existing waste rock dumps. Samples of this material that are crushed to fine particle sizes prior to acid-base accounting tests may exhibit net neutralization potentials significantly different from that of the *in situ* waste material. Having knowledge of mineral coatings would allow one to interpret the test results in a more sound scientific manner. Mineralogical studies also can provide information regarding the sorptive properties of host minerals (e.g., clays) which could allow a determination of whether they are likely to retard the movement of certain contaminants. Studies of mineral compositions could permit identification of the mineralogical sources of trace metals in leachates and provide a basis for designing effective disposal plans.

## 4.2 Physical Considerations

The ability of a material or solid waste to generate acidity or alkalinity, or to contribute metals or other constituents to the environment through leaching, depends partly on the particle-size characteristics of the waste material. Interpretation of test results is complicated if the particle size of the test materials differs significantly from the particle size of a waste material as it is or will be disposed of in the environment. Particle-size characteristics impact both reaction rate and reaction duration by affecting the reactive surface area, the distances between potentially reactive particles, and the porosity and permeability of the waste.

Test materials that are finely ground can impact the results of acid-base accounting tests (Robertson and Broughton, 1992; Lapakko et al., 1998). Crushing to small particle sizes increases the surface area of reactive sulfide and neutralizing minerals. In addition, fine crushing can increase the acid generating potential of a sample by releasing reactive sulfides that are enclosed in inert minerals (e.g., pyrite enclosed in quartz) and which would not be exposed to oxidation in coarser materials (Lapakko et al., 1998). The distance between reactive particles and neutralizing particles is greatly diminished in fine-grained materials, which may inhibit the formation of localized zones of low pH that are known to occur in coarse-grained waste rock piles (Robertson and Broughton, 1992).

The leaching characteristics of waste materials also are affected by changes in particle size. Smaller particle sizes increase the surface area of materials amenable to leaching. Moreover, smaller particle diameters and a smaller range of particle sizes (better grading) affects pore sizes and permeability, both of which influence the volume of extraction fluid held in the pore spaces of granular materials and the amount of time that it is retained by the material.

## 4.3 Acid Generation Potential

Materials that contain iron sulfide minerals such as pyrite, marcasite, or pyrrhotite can generate acid if exposed to moisture (for example, humid air) and an oxidant (either oxygen from the atmosphere or a chemical source such as ferric iron). In addition, some sulfate minerals, such as jarosite, can dissolve to form acidic solutions (e.g., Lapakko, 1991). Bacteria commonly accelerate the process of acid generation from sulfides by enhancing the rate of ferrous iron oxidation (e.g., Kleinman and Erickson, 1983) or the rate of reduced-sulfur oxidation (BC AMD Task Force, 1989). The rate at which acid is generated depends on the composition of the sulfide mineral (e.g., Lundgren and Silver, 1980), its crystal size and shape (surface area; Caruccio et al., 1977), the presence of reaction coatings that may form on the surfaces of sulfide minerals (Goldhaber, 1983; Nicholson et al., 1990; Sherlock et al., 1995), and the environmental conditions (for example, pH, humidity, oxygen fugacity, temperature) at the site of oxidation (BC AMD Task Force, 1989). In general, acid generation involves a rather complex set of chemical reactions that change through time (BC AMD Task Force, 1989).

The potential for acid generation is offset by the ability of a material to neutralize acid. Acid neutralization is imparted by various minerals including calcium- and magnesium-bearing carbonates, oxides and hydroxides of calcium, magnesium, and aluminum, some silicate minerals, and some phosphates (Sherlock et al., 1995). In general, dissolution rates (and hence

neutralization) are considerably faster for carbonate minerals than for other neutralizing minerals. Factors that influence mineral dissolution rates include pH, dissolved carbon dioxide content, temperature, mineral composition, crystal size and shape, redox conditions, and the concentration of “foreign” ions (e.g., trace metals) (Sherlock et al., 1995).

Static predictive tests are used to define the balance between potentially acid-generating minerals and potentially acid-neutralizing minerals in a sample (BC AMD Task Force, 1989). These tests, which are quick and comparatively inexpensive, cannot be used to predict the quality of effluent that may drain from waste materials in the future. However, they are useful for determining which geologic units have the potential to generate acidity and, in essence, serve as positive/negative indicators of the theoretical potential for acid generation (Robertson and Broughton, 1992). When coupled with mineralogical and petrological data from the test samples, certain static test procedures can provide some measure of neutralization rate (Mills, 1998a). Kinetic tests are used to define reaction rates through time under specific environmental conditions. These tests are significantly more expensive and may take months or years to complete.

In general, acid mine drainage testing programs utilize a two-step approach in which static tests of numerous samples are used to identify potentially acid-generating geologic units and to characterize the variability that occurs within them. Kinetic tests are then run on samples deemed representative of the range of compositions within potentially reactive units to determine whether acid drainage will occur. Although New Mexico (NMED, 1996) and Nevada (NV DEP, 1990; 1996) have specific guidelines mandating static and kinetic testing of mine wastes, the states of EPA Region 10 have not adopted a similar approach.

### **4.3.1 Static Tests**

Static test methods, which were developed initially to determine the potential for acid generation from coal mine wastes, have been adapted for use in the metal mining industry. The variety of static test methods that are available are collectively referred to as acid-base accounting (ABA) analyses. Static test methodologies are described and evaluated in reports by Lapakko (1991; 1992), Lawrence and Wang (1996), and Mills (1998a; 1998b); digestion methods are compared and evaluated in Skousen et al. (1996). Table C-1 summarizes several of the more commonly used test methods.

#### **4.3.1.1 Acid-Base Accounting Tests**

Specific procedures for conducting acid-base accounting (ABA) tests are compiled in Mills (1998a; 1998b). Although a few tests produce a single value that can be used to indicate the likelihood for acid generation (Section 4.3.1.2), most static tests determine separate values for the acid generating potential (AP) and acid neutralizing potential (NP) of a sample. These values, expressed in units of tons of  $\text{CaCO}_3$  equivalent per kiloton of material, are used together to indicate whether a sample has a stoichiometric balance that favors net acidity or net alkalinity. In general, determinations of acid generating potential are relatively straightforward. This is not true of tests to measure neutralizing potential. The problem stems from the widely variable solubilities and reaction rates of minerals that have the potential to neutralize acidity (e.g.,

carbonates vs. silicates), the relative differences in aggressiveness of the various methods used to determine neutralization potential, and the different titration endpoints employed by each test (e.g., Mills, 1998a). Studies in which the neutralizing potential of a sample was determined using different methods concluded that the NP value is highly sensitive to test methodology (e.g., Lapakko, 1994). Consequently, it is important that any program established to test wastes and materials prior to or during operation use a single test method to ensure that the program produces data that are internally consistent.

#### 4.3.1.1.1 Methods to Determine Acid Generating Potential

Acid generating potential is determined from the sulfur content of a sample (expressed in weight percent). This value is converted to acid generating potential (AP) by multiplying by a factor of 31.25 that is derived from the molar stoichiometry of the oxidation and neutralization reactions. The conversion factor assumes that all reported sulfur occurs as pyrite, that pyrite is completely oxidized to sulfate and ferric hydroxide, and that hydrogen ions produced in the oxidation reaction are neutralized by  $\text{CaCO}_3$ . Acid generating potential is reported in kilograms of  $\text{CaCO}_3$  equivalent per metric ton of sample (also expressed in units of metric tons of  $\text{CaCO}_3$  equivalent per kilotonne of material).

Samples typically contain sulfur in more than one form, not all of which are capable of generating acidity. The sulfur speciation tests of Sobek et al. (1978) are the most commonly used methods to determine sulfur content. Alternative methods include the hydrogen peroxide method (O'Shay et al., 1990) and reactive sulfur tests.

Sobek et al. (1978) describe procedures to determine the total sulfur, HCl-extractable sulfate sulfur,  $\text{HNO}_3$ -extractable sulfide sulfur, and organic sulfur contents of a sample. The tests require a sample crushed to particle sizes smaller than 60 mesh (0.25 mm), which is split into three parts that are analyzed for total sulfur using a Leco sulfur analyzer. One split is left untreated and provides a measure of the total sulfur content of the sample. A second split is leached with HCl and a third split is leached with  $\text{HNO}_3$ . Acid-extractable sulfate sulfur (e.g., gypsum and anhydrite) is computed from the difference between the total sulfur contents of the untreated and HCl-treated splits. Acid-soluble sulfide sulfur (e.g., pyrite) is computed from the difference between the total sulfur contents of the HCl-treated and  $\text{HNO}_3$ -treated splits. Nonextractable organic sulfur is computed as the total sulfur content of the  $\text{HNO}_3$ -treated split. The test methods have disadvantages that include the potential removal of highly reactive sulfide by HCl and the potential nondetection of sulfide that is slow to oxidize under experimental conditions, but which may form acid in the environment (BC AMD Task Force, 1989).

It is important to recognize that sulfur speciation tests like those described above do not distinguish acid-insoluble sulfates, such as barite or jarosite, which will report as sulfide sulfur. As a result, samples containing significant quantities of these minerals will appear to have more sulfide sulfur than they actually do. Although acid-insoluble sulfates will not oxidize to produce acid, some of these minerals (e.g., jarosite, alunite, and melanterite) may dissolve, hydrolyze, and generate acidity (Carson et al., 1982; Mills, 1998a). Mills (1998a) states that whole-rock barium concentrations can be used to correct sulfide sulfur determinations when barite is present. However, barium also may be present in common alteration phases such as potassium feldspar

and biotite (Deer et al., 1992). Consequently, caution must be used when applying a barium correction of this type. As pointed out by Mills (1998a), it is rarely acknowledged that each step in the sulfur speciation tests introduces analytical error; these errors are cumulative.

Table C-1. Summary of Commonly Used Static Test Methods.

Static Test Method	Reference	Comments
Sobek	Sobek et al. (1978)	AP uses sulfur speciation and Leco analyzer. NP uses fizz test and heated HCl that dissolves carbonates and most silicate minerals; NaOH titration endpoint of 7.0. This is an aggressive test that provides “best case” values.
Modified Sobek NP	Lawrence and Wang (1997)	NP uses fizz test and HCl at ambient temperature that dissolves carbonates and reactive silicate minerals; NaOH titration endpoint of 8.3. Less aggressive test due to use of ambient temperature acid. Lapakko (1992) suggested that the alkaline titration endpoint may lead to overly optimistic estimates of NP.
Sobek NP Siderite Correction	Skousen et al. (1997)	NP uses fizz test and heated HCl; hydrogen peroxide added prior to titration to oxidize ferrous iron from dissolved siderite. Yields less alkaline NP than standard Sobek method when siderite is abundant.
BCRI Initial	Duncan and Bruynesteyn (1979)	AP uses total sulfur by Leco furnace or wet chemistry. NP uses H <sub>2</sub> SO <sub>4</sub> added to pH 3.5 at ambient temperature that dissolves carbonates and possibly limonite and chlorite; gives “most likely case” values.
Lapakko NP	Lapakko (1994)	NP uses H <sub>2</sub> SO <sub>4</sub> added to pH 6.0 at ambient temperature for up to 1 week that dissolves carbonates; gives “worst case” value.
Net Acid Generation (NAG)	Miller et al. (1997)	Crushed sample is boiled with hydrogen peroxide then titrated to pH 4.5 with NaOH. NAG value, expressed in units of kg H <sub>2</sub> SO <sub>4</sub> /tonne, provides indication of potential for net acidification.
Paste pH	Sobek et al. (1978) Page et al. (1982)	Sample is mixed with water and pH measured by meter. pH value provides indication of potential for net acidification.
Summaries include information from Mills (1998a and 1998b).		

The hydrogen peroxide method (O'Shay et al., 1990) has been used to determine the pyrite content of coal mine wastes. In this test, a sample crushed to particle sizes smaller than 150 microns is soaked in HCl for two hours to remove carbonate minerals. The treated sample is mixed with hydrogen peroxide and pH is monitored at intervals of 1 to 2 minutes. Curves of pH versus time are compared to curves generated from synthesized standards. Potential acidity is determined using the conversion factor of 31.25.

Reactive sulfur tests treat sample splits with hydrogen peroxide to oxidize sulfide minerals to sulfates. The sulfate content of the peroxide leach solution is used to determine the amount of reactive sulfur, which is converted to potential acidity using the conversion factor of 31.25. Producing accurate results with this test method, which is not widely used, requires strict temperature control (Hinnert and SAIC, 1993), because pyrite decomposition is exothermic.

#### 4.3.1.1.2 Methods to Determine Acid Neutralizing Potential

A variety of procedures are used to determine the neutralizing potential of a sample (Table C-1). In general these methods involve reacting a sample with a known quantity of acid, determining the base equivalent amount of acid consumed by the sample, and converting measured quantities to neutralization potential (NP), which is expressed in units of tonnes of  $\text{CaCO}_3$  equivalent per kilotonne of material (Mills, 1998a).

The Sobek and Modified Sobek methods, which are perhaps the most widely used procedures, both use a “fizz test” to determine the quantity of acid that will be used in the NP determination. In essence, the test consists of adding a small amount of acid to a small quantity of test sample and subjectively assigning a fizz rating of “no”, “slight”, “moderate”, or “strong” to the resulting effervescence. Each of these ratings corresponds to a different quantity and/or normality of acid that is added to the sample (Sobek et al., 1978). Lawrence and Wang (1996) and Skousen et al. (1997) conducted studies to examine the effects of assigning different fizz ratings when determining Sobek NP values for a variety of samples. Their results showed that NP values could differ by amounts that varied from a few percent to a few hundred percent for one or two category changes in fizz rating.

Neutralization potential (NP) by the Sobek and Modified Sobek methods is determined by treating the sample with an excess of hydrochloric acid and then titrating with sodium hydroxide to determine the amount of unconsumed acid. In the original test procedure outlined by Sobek et al. (1978), the sample is reacted with hot acid and titrated to a pH of 7. In the Modified Sobek procedure outlined by Coastech Research (1989), the sample is agitated with acid at room temperature for 24 hours and titrated to a pH of 8.3 (cf., Lawrence and Wang, 1997). In both cases, the amount of titrated base is converted to a calcium carbonate equivalent in units of kilograms per metric ton of sample (also expressed in units of metric tons of  $\text{CaCO}_3$  equivalent per kiloton of material).

The Sobek and Modified Sobek tests determine the maximum amount of neutralization potential available in a sample, but do not predict the rate of neutralization nor indicate the pH to which a sample can neutralize acidity. Lapakko (1992) showed that both tests provided a fairly reliable estimate of NP for samples composed of quartz, alkali feldspar, and mica, but overestimated NP in samples with abundant calcic feldspar, chlorite, clay, pyroxene and olivine. Similar conclusions were drawn by Skousen et al. (1996) who showed that NP estimates for a single sample could vary by an order of magnitude depending on sample mineralogy and digestion method. Other criticisms of the Sobek and Modified Sobek methods (see Lapakko, 1991; 1992 and Hinnert and SAIC, 1993) include: 1) the small particle size used in the tests may produce unrealistically high values for NP, 2) hot acid which is mixed with water and heated to boiling in the Sobek method may increase analytical scatter, 3) hot acid may digest siderite (iron



carbonate) and clay minerals that increase NP values but provide little alkalinity, 4) NP may be overestimated because pH is back-titrated to values of 7.0 or 8.3, not 6.0 which is a typical water quality standard, and 5) NP may be overestimated if metal hydroxides precipitate during the addition of the sodium hydroxide base.

The BCRI Initial test (Duncan and Bruynesteyn, 1979; Bruynesteyn and Hackl, 1984) and Lapakko NP test (Lapakko, 1994) both use sulfuric acid at ambient temperature to determine neutralizing potential; neither test requires a subjective fizz test rating. In both tests, the sample is suspended in water and acid is titrated into the suspension until a stable, pre-determined pH value is achieved. The BCRI Initial test uses a titration endpoint of 3.5, whereas the Lapakko NP procedure uses a titration endpoint of 6.0. The volume of titrated acid is used to compute a value for acid consumption, which is expressed in units of kilograms per tonne. Neither test is particularly aggressive in dissolving minerals in addition to the carbonates. Nevertheless, the higher titration endpoint of the Lapakko procedure makes it the most conservative (lowest NP estimate) of the static NP test procedures. Lapakko (1992) showed that the BCRI test overestimated NP for samples containing significant siderite (iron carbonate).

Two alternative methods have been developed to determine neutralizing potential, although they apparently are not in widespread use. The alkaline production potential test was developed for use by the coal mining industry. In this method, a sample crushed to minus 23 microns is mixed with HCl and allowed to react for two hours at room temperature. The mixture is then titrated to pH 5.0. Although this method reduces dissolution of less reactive carbonate minerals (e.g., siderite), it may not permit reaction of all of the buffering carbonates present in the sample (Coastech Research, 1989). During the carbonate analysis test, a sample is digested in acid in a sealed chamber. The carbon dioxide (CO<sub>2</sub>) gas evolved by reaction is absorbed into a basic solution and measured using a Leco analyzer (BC AMD Task Force, 1989). The carbonate content of the sample is determined from the amount of CO<sub>2</sub> gas evolved, with the result converted to CaCO<sub>3</sub> equivalent. This test offers the advantage of determining only the carbonate minerals capable of neutralizing pH to 5.9. However, the test cannot be used if a sample contains significant pyrrhotite (Fe<sub>1-x</sub>S), because this mineral will react to form sulfur dioxide gas that interferes with the Leco analyzer (BC AMD Task Force, 1989).

#### **4.3.1.2 Static Tests that Produce a Single Indicator Value**

Two test procedures have been developed that provide a means for quickly indicating whether a sample is likely to have a stoichiometric balance that favors acid production. The net acid generation (NAG) test (Miller et al., 1997) uses a peroxide solution to oxidize sulfide minerals to sulfates. The oxidation process produces acid which reacts with alkaline minerals in the sample. Upon complete reaction, the solution is titrated to pH 4.5 using NaOH. The volume of titrated NaOH is used to compute a NAG value, which is expressed in units of kg of H<sub>2</sub>SO<sub>4</sub> per metric ton of material.

Paste pH is a simple and inexpensive method to indicate the presence of reactive carbonate or readily available acidity. In this test, powdered rock and water are mixed in a specific ratio to form a paste. The pH of the paste is determined using a pH meter and pH

reference electrode assembly. The test offers no indication of the relative proportions of acidifying or neutralizing components in a sample (BC AMD Task Force, 1989).

#### 4.3.1.3 Interpreting Static Test Results

Static test results provide a preliminary indication of whether a sample is likely to produce acidic drainage in the environment. These tests do not, however, provide any data regarding when acidification may occur or the rates at which acid generation and neutralization reactions will proceed. As such, they are useful only for screening samples for their potential behavior. It should be kept in mind that most static tests are conducted using crushed or pulverized samples that may have particle sizes significantly smaller than materials as they will be disposed of. This can significantly change the chemical availabilities of reactive minerals as described in Section 4.2. In addition to these factors, interpretations should incorporate knowledge of sample mineralogy.

Static test results are generally interpreted within an empirically developed framework established from experience in the coal mining industry. Interpretations are based on the net neutralization potential and ratio of neutralizing potential to acid generating potential. The values given in Table C-2 provide general guidelines for interpreting static test results and they should be viewed in light of the sulfur content of the sample (some samples may not contain enough pyritic sulfur to produce a quantity of acid sufficient to degrade the environment even in the absence of neutralizing materials). Because exceptions to these guidelines can and do occur, kinetic tests should be conducted to confirm the static test results.

Many static test interpretations use a value for acid generating potential computed from the total sulfur content of a sample because it provides the most conservative (highest AP value) measure of acidification potential. In contrast, sulfide sulfur values provide more realistic, but less conservative, estimates of acid generating capability because these analyses do not report sulfur in forms that are not acid generating (e.g., gypsum). The Canadian metal mining industry has adopted the use of sulfide sulfur as its standard method to compute acid generating potential (Mills, 1998a). It should be recognized that the assumptions inherent in the derivation of the stoichiometric conversion factor lead to additional uncertainty, since the factor could be significantly greater or less than 31.25 (BC AMD Task Force, 1989; see Section 4.3.1.1.1). In fact, some workers advocate using a value of 62.5 (Brady et al., 1990).

Table C-2. Suggested Guidelines for Static Test Interpretation.

	Potentially Acid Generating	Uncertain Behavior *	Potentially Acid Neutralizing
NP - AP	< -20 tonnes/kilotonne	> -20 to < +20 tonnes/kilotonne	> + 20 tonnes/kilotonne
NP/AP	< 1	1 to 3	> 3
* Samples exhibiting uncertain behavior should be tested kinetically.			

The net neutralizing potential (NNP), which is defined as the difference between the acid neutralizing potential (NP) and acid generating potential (AP) of a sample, is computed by subtracting the latter from the former (NP-AP) when both are expressed in units of kilograms of  $\text{CaCO}_3$  equivalent per metric ton of material (or metric tons per kiloton). In general, samples with NNP exceeding +20 kg/tonne are considered to be non-acid-generating (Robertson and Broughton, 1992). In contrast, samples with NNP less than -20 kg/tonne are considered to be potentially acid generating (Robertson and Broughton, 1992). Samples with NNP values between these two cutoffs occupy an area of uncertainty and should be tested kinetically to determine their acid generating capability (Robertson and Broughton, 1992). Although the +/-20 cutoff values are generally accepted by most workers, some researchers have advocated less stringent values for some mine wastes (see discussions in Lapakko, 1991; 1992 and Hinners and SAIC, 1993).

The ratio of acid neutralizing potential to acid generating potential (NP/AP) also is computed from static test results when both are expressed in units of kilograms of  $\text{CaCO}_3$  equivalent per metric ton of material (or metric tons per kiloton). In general, samples with NP/AP exceeding 3 are considered to be non-acid-generating (Robertson and Broughton, 1992). In contrast, samples with NP/AP less than 1 are considered to be potentially acid generating (Robertson and Broughton, 1992). Samples with ratios between these two cutoffs occupy an area of uncertainty and should be tested kinetically to determine their acid generating capability.

#### 4.3.1.4 State Recommendations

The States comprising EPA Region 10 presently have not established formal regulatory guidelines for conducting static tests of mine wastes and materials. The State of Nevada (NV DEP, 1990) recommends use of the Sobek et al. (1978) method to determine neutralization potential and either the Sobek et al. (1978) or the peroxide method (presumably O'Shay et al., 1990) to determine acid generating potential. Those samples in which NP exceeds AP by 100 percent (NP/AP >2) are considered non-acid generating and do not require additional testing (NV DEP, 1990). Samples that do not meet this criteria should be tested kinetically. The State of New Mexico recommends determining the acid potential of representative samples using total sulfur and the neutralization potential using either the ABA, modified ABA, BCRI, or alkaline production methods (NMED, 1996). Kinetic tests are suggested for those samples with NP/AP ratios less than 3. Samples with ratios exceeding 3 are considered non-acid generating. The states of Nevada and New Mexico illustrate that states may view different test methodologies as acceptable. Applicants should check with state agencies to determine whether they have preferences that may not be codified.

#### 4.3.2 Kinetic Tests

Kinetic test procedures are designed to accelerate the natural weathering process in order to provide information about the rates of acid consumption and acid production over time. A variety of kinetic test methods are available, including conventional and modified conventional humidity cells, SRK humidity cells, soxhlet extractions, column leach tests, shake flask extractions, modified B.C. Research tests, simulated environment studies, and field lysimeter tests; humidity cells and columns are most commonly used by the mining industry. According to

Lapakko (1991), there is no single test that produces all of the chemical information needed to evaluate all mine wastes under all conditions of disposal. Most of the kinetic testing procedures are complex, time-consuming, and require considerable operator skill to produce consistent results.

#### 4.3.2.1 Kinetic Test Methods

The various kinetic tests described below are similar to one another in that a sample is subjected to periodic leaching, the leachate is collected and analyzed, and rates of acid generation, metals release, and neutralization capacity depletion are computed. The methods differ in the amount of sample used in the test, the particle size of the tested material, test conditions (lab vs. field), and test duration. Although not specifically stated in most procedures, it is typical for splits of the starting sample and final leached product to be tested for static acid-base properties and total metals; mineralogical analyses also should be conducted on these samples because these data can provide important constraints to assist the interpretation of test results (Mills, 1998c).

##### 4.3.2.1.1 Conventional and Modified Conventional Humidity Cells

The conventional humidity cell (Sobek et al., 1978) is a bench-scale test that uses a comparatively small amount of sample (200 to 300 g) crushed to particle sizes smaller than 2 mm. A split of the sample is analyzed for metals and other constituents to assist in the evaluation of water quality from the tests. The sample is placed in a sealed plastic box and dry air is passed over the sample for 3 days, followed by moist air for 3 days. Every seventh day, the sample is flushed with a specified volume of water. To simulate the composition of regional acidic rain, the pH of the water may be adjusted to slightly lower pH. The leachant is collected and analyzed for sulfate, pH, acidity, alkalinity, and electrical conductivity. This 7-day process is repeated for 10 weeks, although some samples may require a longer reaction period (Coastech Research, 1989). Test durations of 20 weeks are used commonly in the metal mining industry (see discussion in Section 4.3.2.2).

The modified conventional humidity cell designed by Lawrence (1990) uses a bigger sample size and larger volume of water for the flush cycles. The test is conducted in a manner generally similar to the Sobek method.

ASTM procedure D5744-96 (ASTM, 1998), which was designed specifically for mining wastes and materials, uses a modified column as a humidity cell. The test is conducted on a kilogram of sample crushed to particle sizes smaller than 6.3 mm. The test is run for 20 weeks in a manner similar to the Sobek method, with 3 days of dry air, 3 days of moist air, and a weekly flush with 0.5 or 1.0 liter of water. The procedure includes provisions for pre-leach and post-leach mineralogical and chemical characterization of the solid sample and directions for preparation and use of an optional bacterial (*T. ferrooxidans*) spike.

Few data are available to document the reproducibility of humidity cell data (Mills, 1998c). Experiments designed to test the validity of conventional humidity cell results for tailings and waste rock samples are summarized in Lapakko (1991; 1992). In general, the

conventional humidity cell is able to indicate many of those samples that become acid producing. However, some validation tests noted indefinite pH trends that were difficult to interpret and some tests failed to predict acid generation, suggesting that these experiments should have continued for longer durations to permit depletion of the neutralizing capacity. Criticisms of the conventional humidity cell are given in Broughton and Robertson (1992). These authors argue that the small particle size used in the tests masks the influence of particle size on acid generation, making them unsuitable for waste rock samples; however, the particle sizes used in the tests are similar to tailings. Moreover, they point out that the complete sample flush may affect the development of local low pH and disrupt the natural storage and flushing of oxidation products. Other workers, however, feel that the small particle size is not a limiting factor since the most highly reactive products in waste rock piles typically occur in the smaller size fractions (Hinnert and SAIC, 1993). For existing waste rock dumps, Price (1997) recommends using only the sub-2 mm size fraction of (i.e., crushing larger clasts should be avoided) in humidity cell tests. For proposed waste rock dumps, Price (1997) recommends crushing drill core material to 80% less than 6 mm. Clay-rich samples can pose problems for humidity cell testing because the clay particles can be easily lost during weekly flushing and they can clog filters used to prevent the loss of fine materials (Mills, 1998c).

#### **4.3.2.1.2 SRK Humidity Cells**

Broughton and Robertson (1992) present a modified humidity cell (termed the SRK humidity cell) designed to test coarse waste rock samples. This test uses material crushed to sizes smaller than 10 cm which is placed into a cylindrical column with a diameter of 30 cm and height of 45 cm. Humid air is cycled constantly through the cell. Flush water is introduced at several points along the upper surface of the waste rock so that it percolates downward along discrete pathways. The volume of flush water approximates (per unit area) conditions encountered in the field. The cells can be stacked to allow leach water from one test cell to be used as flush water in an underlying cell.

The SRK design eliminates complete flushing of the oxidation products, permitting local areas of low pH to develop within the cell (Broughton and Robertson, 1992). The coarse size fraction more closely approximates the separation distance between acid-producing and acid-neutralizing minerals in waste rock samples.

#### **4.3.2.1.3 Soxhlet Extractions**

Soxhlet reactors recirculate water or other fluids through a sample to simulate conditions of weathering. The method of Sullivan and Sobek (1982) uses distilled water at 25EC to leach a sample over a period of six weeks, although the test duration can vary. A technique described by Renton et al. (1988) uses as the leach material a pulverized coal waste sample that has been oxidized in an oven. The sample is leached in a soxhlet reactor with distilled water at 85EC and the leachate is analyzed for water quality parameters. The sample is returned to the oven for additional oxidation prior to the next leach cycle. The oxidation-leaching cycle is repeated 5 times.

Soxhlet extractions require sophisticated equipment and considerable operator skill, especially for the Renton et al. procedure. Evaluations of the Sullivan and Sobek (1982) method by Coastech Research (1989) indicate that it may provide reliable results for tailings samples. The aggressive oxidation of samples and elevated leaching temperatures used in the Renton et al. method tend to overestimate the acid producing capability of a sample by accelerating the dissolution of carbonate minerals (Bradham and Caruccio, 1990).

#### **4.3.2.1.4 Column Tests**

Column test procedures have not been standardized (Mills, 1998c). Consequently, they are highly flexible tests that permit a range of column designs, test material characteristics, and flow rates. Column tests can be conducted in a manner similar to conventional humidity cells, but they can also be run in an “upflow” mode to simulate subaqueous disposal or as subaerial columns without forced oxygenation (i.e., the top of the column is open but air is not forced through the sample) (Mills, 1998c). Columns, which typically have diameters of 15 cm and lengths of up to 2 m, can be constructed with larger diameters and lengths to accommodate larger sample sizes (10 kg to 3 metric tons; Broughton and Robertson, 1992). Particle sizes up to 2 cm are commonly used in these tests. Materials can be inoculated with bacteria or stratified with neutralizing materials (for example, limestone) to test disposal options.

Subaerial columns are used to simulate the effects of precipitation infiltration into and drainage from materials that are exposed to the atmosphere. A fixed amount of water may be added to the column on a regular basis or the amount may be varied and added irregularly to simulate seasonal variability (Mills, 1998c). Moreover, water may be added to specific portions of the column surface to promote flow along preferred pathways, which allows oxidation products to accumulate on particle surfaces within the column (Mills, 1998c).

Subaqueous columns are used to simulate water infiltration into and drainage from materials that are stored under a water cover. To simulate seepage to ground water, columns can be constructed to permit downward displacement of pore waters by supernatant water (Mills, 1998c). They also can be constructed to allow slow upward movement of deoxygenated water in a manner that simulates submarine disposal.

Experiments designed to determine the validity of column tests for tailings and waste rock samples are summarized in Lapakko (1991; 1992). Several of these studies (e.g., Doepker, 1989) concluded that pyrite oxidized more rapidly in columns that remained unsaturated between flushes, producing lower pH leachate than saturated columns. In general, column tests appear to distinguish potentially reactive materials from benign materials, but the leachant compositions may not reflect what occurs under natural settings (Doepker and O'Connor, 1990).

#### **4.3.2.1.5 Shake Flask Extractions**

Also termed batch reactor tests, shake flask tests utilize a split of powdered sample immersed in distilled water that may be inoculated with bacteria. The flask is sealed and placed on a shaker table where it is vibrated for a period of days to weeks. Samples are removed

periodically and analyzed to determine the sulfate content, pH and other water quality parameters.

The shake flask test is relatively simple and inexpensive. However, for long duration tests, water may need to be added to maintain volume and submersion of the sample may inhibit oxidation of reactive sulfides (BC AMD Task Force, 1989). Interpretation of test results is quite complex if water has been added periodically.

#### **4.3.2.1.6 Field Tests**

Field lysimeter tests are conducted using sample quantities that vary from barrel-scale to piles. The tests can be conducted for protracted periods (years) under natural climatic conditions. In cases where samples have a small to moderate amount of neutralization potential, long test durations are required to overcome the effects of neutralization and the lag period that precedes bacterial oxidation (Lapakko, 1991). Test piles are typically equipped with lysimeters or set atop impermeable liners to facilitate collection of drainage samples and are constructed in a manner similar to actual or proposed waste rock or tailings piles. Drainage volumes and concentrations can be used to calculate the mass release rates of metals per unit mass of waste.

A major advantage of field tests is their conduct under the environmental conditions at the disposal site, which provides more realistic estimates of water quality and the rates of acid generation and neutralization than bench-scale lab tests. In addition, they allow control options, such as limestone addition (Humphreys, 1990), to be tested under natural conditions. However, it is critical that the tests be conducted for durations of sufficient length to smooth the effects of short-term climatic variations. Consequently, their long duration makes these tests difficult to use, especially for evaluating proposed actions.

#### **4.3.2.2 Interpreting Kinetic Test Results**

The interpretation of kinetic test results, for which accepted criteria are generally lacking, can range from relatively straightforward to extremely difficult (Ferguson and Erickson, 1988; Mills, 1998d). All interpretations should be based on knowledge of sample mineralogy, static test data, particle size characteristics, and water flow (Mills, 1998d). Scaling issues are a significant obstacle when using bench-scale kinetic test results to quantitatively estimate acid generation in waste rock and tailings piles. Included are the effects of grain size and reactive surface area, infiltration rates, and flushing rates and volumes (see comments in Hinners and SAIC, 1993).

Most investigators use temporal trends in leachate quality, including pH, sulfate, acidity, alkalinity, and trace metals, to identify the progression of the acid mine drainage process (e.g., Ferguson and Erickson, 1988; Lapakko et al., 1995; Mills, 1998d). Because trends in leachate composition reflect changing sample mineralogy and geochemical equilibrium conditions, they must be interpreted cautiously. Equilibrium chemical speciation programs, such as MINTQA2 (Section 5.2.2), can be used to identify the precipitation/dissolution reactions that are likely to control leachate composition. It is important to keep in mind that lab-scale kinetic tests are specifically designed to accelerate the natural weathering process. Consequently, these tests

cannot be used to determine when materials may begin to generate acid in the environment (only that they will or will not), and they generally will produce leachates with higher metal concentrations than would be produced naturally (Mills, 1998c). For most bench-scale tests, samples are considered strongly acid generating if leachate pH falls below 3; acid generating with some neutralization occurring if pH is between 3 and 5; and not significantly acid generating (or generated acid is overwhelmed by excess alkalinity) if solution pH exceeds 5 (BC AMD Task Force, 1989; Humphreys, 1990).

Sample mineralogy plays a pivotal role in controlling leachate quality (Mills, 1998d). For samples lacking sulfate minerals, the production of aqueous sulfate may be used to monitor the sulfide oxidation process. In contrast, when gypsum or other soluble sulfate minerals are present, their dissolution will provide aqueous sulfate that can mask sulfate produced by sulfide oxidation. In some cases, high aqueous sulfate concentrations produced by gypsum dissolution may delay the onset of sulfide oxidation in kinetic tests (Mills, 1998d). Test samples collected from existing waste piles may contain previously formed oxidation products that dissolve at varying rates to contribute metals to kinetic test leachates. Hydrolysis of these metals can lead to reduced pH. Depending on reaction kinetics, secondary mineral dissolution is likely to overprint the effects of sulfide oxidation, which complicates calculations of sulfide oxidation rates (Mills, 1998d).

Whether kinetic test samples may eventually begin to produce acidic leachates depends on the proportions of acid generating and acid neutralizing materials, their relative dissolution and reaction rates, and the particle size characteristics of the test materials. Kinetic test duration is a critical issue. Kinetic tests must be conducted for a period of time that is sufficient to permit the dissolution of neutralizing minerals and accumulated oxidation products and to overcome the lag-time that precedes the onset of bacterial oxidation. Although 20-week test lengths are common in the metal mining industry, there is a growing trend toward longer test times. For example, Price (1997) recommended minimum test durations of 40 weeks and Mills (1998c) reported that test lengths commonly exceed 104 weeks in western Canada. In long-term studies reported by Lapakko et al. (1998), some samples did not begin to produce acidic drainage until more than two years into the kinetic tests. Particle size also strongly influences kinetic test results. The reduced particle sizes used in many bench-scale tests enhance reactivity by liberating sulfides enclosed in silicate minerals (e.g., pyrite enclosed in quartz; Broughton and Robertson, 1992; Lapakko et al., 1998; Mills, 1998e). In coarser samples, these sulfides would not be exposed to oxidation. Moreover, smaller particle diameters increase the total surface area of acid generating and acid neutralizing minerals exposed to reaction which, in turn, affects reaction rates and drainage quality (Lapakko et al., 1998; Mills, 1998c).

Finally, it is important to consider that differences between lab test conditions and the natural environment are likely to complicate extrapolation of kinetic test results. Differences between lab and ambient atmospheric temperature, lab wetting cycles and natural precipitation frequency, and complete flushing flows in the lab vs. incomplete or channelized flow in actual waste piles are cited by Mills (1998c) as factors that require consideration.

#### 4.3.2.3 State Recommendations



The states comprising EPA Region 10 presently have not promulgated formal guidelines that cite specific kinetic procedures. The State of Nevada accepts kinetic testing methods that include shake flask extractions, soxhlet extractions, conventional humidity cells, column tests, and field tests (NV DEP, 1990). Although kinetic tests are required for samples of spent ore, tailings, and waste rock, the State does not provide guidelines for the interpretation of test results. The State of New Mexico recommends the use of humidity cells and columns for most kinetic test applications, but will accept soxhlet extraction test results as appropriate (NMED, 1996). The State recommends shake flask extractions for simulating closure conditions that require underwater storage (NMED, 1996). The State does not provide criteria by which to interpret kinetic test results. Applicants should check with state agencies to determine whether they have preferences that may not be codified.

#### **4.3.3 Mathematical Models**

Neither static nor kinetic test results provide the types of data that determine unequivocally the potential for acid generation from waste rock and tailings piles. Instead, test results must be extrapolated to longer time frames and different environmental conditions and scaled to account for the differences in waste volumes, particle sizes, particle separation distances, infiltration rates, flushing rates, and flushing volumes between laboratory test samples and waste deposits. Mathematical models can help to bridge this gap and can help planners determine the potential effects of waste rock and tailings piles runoff.

Empirical models of acid generation utilize trends observed in test results to extrapolate future conditions, typically using “best-fit lines” through test data points (BC AMD Task Force, 1989). The accuracy of an empirical model, which is by definition a site-specific model, depends on the quality of the test data. Major sources of uncertainty include differences in particle-size distributions between test materials and actual waste materials and lack of model calibration to conditions as they will exist in the waste disposal setting (BC AMD Task Force, 1989).

Theoretical or deterministic models solve a series of equations that represent different physical or chemical aspects of the acid generation process in order to predict the temporal evolution of acid generation (see Perkins et al. [1995] for a review of the application of geochemical models to predictions of acid generation). Models include the Reactive Acid Tailings Assessment Program (RATAP) model (SENES and Beak, 1986; 1988); the mine tailings oxidation (MINTOX) model (MEND, 1997); the sulfide oxidation model of Davis and Ritchey (1986); and the MINEWALL model (MEND, 1995). RATAP was developed to assess acid generation and ground water quality in fine-grained pyritic tailings. MINTOX can be used to predict the kinetic behavior of sulfide oxidation within mine tailings impoundments and simulate the speciation and transport of oxidation products through tailings and into downstream aquifers. The Davis and Ritchey model determines an approximate analytical solution that allows a user to evaluate the amount of time required for oxidation of all material in a mass of waste and estimate the amount of time that materials can pose a threat in the environment. The MINEWALL model can estimate water chemistry continuously through operational and closure phases of a mining operation.

Uncertainty is introduced into theoretical models by an incomplete understanding of the system which is being modeled or through use of simplifying assumptions (BC AMD Task Force, 1989). In general, theoretical models may fail to properly describe fluid transport through constructed waste piles, accurately predict thermal gradients that may arise due to the oxidation process, and correctly determine the transport of oxygen and reaction products in compositionally and physically heterogeneous wastes (BC AMD Task Force, 1989; Nicholson, 1992).

## **4.4 Leaching Procedures**

Spent ore, waste rock, or tailings materials that are exposed to the environment can potentially contribute metals or other contaminants to the environment. Metals can be leached from geological materials even under neutral conditions, but it is accelerated by materials that generate acid as a consequence of sulfide oxidation. Consequently, a variety of leaching tests are used to determine which constituents in waste materials are potentially mobile under the expected environmental conditions.

### **4.4.1 U.S. EPA Procedures**

EPA has developed three leach test procedures. Of these, the Synthetic Precipitation Leaching Procedure (SPLP) test and Toxicity Characteristic Leaching Procedure (TCLP) test are the most widely applied by the mining industry. The SPLP test is most applicable to metals removal from mining wastes and materials.

#### **4.4.1.1 EP Toxicity Test**

The Extraction Procedure (EP) Toxicity Test (EPA Method 1310A) was developed to determine whether a particular waste material exhibits the characteristics of a hazardous waste. The method, which has been replaced by the TCLP test for regulatory purposes, is outlined in U.S. EPA (1986a), with the most recent version of the experimental procedure dated July 1992, revision 1. The method uses an extraction fluid composed of acetic acid diluted to pH  $5.0 \pm 0.2$ . Solid samples of approximately 100 g are crushed to sizes smaller than 9.5 mm and placed into an extraction bottle; special procedures are used for mixed solid/liquid waste. A 16:1 weight ratio of extraction fluid:sample solid is added to the bottle, which is agitated for 24 hours. Following extraction, the leachate is filtered and analyzed for metals.

#### **4.4.1.2 Toxicity Characteristic Leaching Procedure Test**

The Toxicity Characteristic Leaching Procedure (TCLP) Test (EPA Method 1311; ASTM Method D5233) was designed to evaluate the mobility of inorganic and organic constituents in liquids, solids, and mixed wastes in a sanitary landfill. The method is outlined in U.S. EPA (1986a), with the most recent version of the experimental procedure dated July 1992, revision 0. For non-alkaline materials, the method uses an extraction fluid composed of acetic acid diluted to pH  $4.93 \pm 0.05$ . For alkaline materials, the method uses an extraction fluid composed of acetic acid diluted to pH  $2.88 \pm 0.05$ . Samples containing volatile organic components are leached using a zero head space tumbler and the pH 4.93 extract fluid. For non-volatile materials, samples of approximately 100 g are crushed to sizes smaller than 9.5 mm and placed into an

extraction bottle. A 20:1 weight ratio of extraction fluid:sample solid is added to the bottle, which is agitated for  $18 \pm 2$  hours. Following extraction, the leachate is filtered, preserved with nitric acid, and analyzed for metals.

#### **4.4.1.3 Synthetic Precipitation Leaching Procedure Test**

The Synthetic Precipitation Leaching Procedure (SPLP) test (EPA Method 1312) was designed to determine the mobility of organic and inorganic analytes in liquids, solids, and mixed wastes using a batch leach technique. The method is outlined in U.S. EPA (1986a), with the most recent version of the experimental procedure dated September 1994, revision 0. For areas west of the Mississippi River, the method uses an extraction fluid composed of a 60/40 weight percent mix of sulfuric/nitric acid diluted to  $\text{pH } 5.00 \pm 0.05$  to simulate regional acidic precipitation. Samples containing cyanide or volatile organic components are leached using special procedures and distilled water as the extraction fluid. For non-volatile materials, samples of approximately 100 g are crushed to sizes smaller than 9.5 mm and placed into an extraction bottle. A 20:1 weight ratio of extraction fluid:sample solid is added to the bottle, which is agitated for  $18 \pm 2$  hours. Following extraction, the leachate is filtered, preserved with nitric acid, and analyzed for metals.

#### **4.4.1.4 Monofilled Waste Extraction Procedure**

The Monofilled Waste Extraction Procedure (MWEP) is a sequential batch extraction test developed to predict the composition of leachate produced from solid waste under field conditions. The procedure is outlined in U.S. EPA (1986b). Solid materials are crushed to pass a 9.5 mm sieve and are combined with extraction fluid in a 10:1 liquid:solid ratio. The mixture is tumbled at room temperature for 24 hours. The procedure uses reagent grade water as the extraction fluid, however, the test can be conducted using process waters, ground waters, or other fluids that occur at a site. Following extraction, the leachate is filtered and analyzed. The solid residue is returned to the extraction vessel and the leach process is conducted using fresh extraction fluid. Four leachings per sample are recommended. Not only does this procedure allow single samples to be leached repetitively, but it permits more than one sample to be leached by the same extraction fluid.

### **4.4.2 State Procedures**

The State of Nevada recently developed a leach test specifically for mining wastes. The procedure has been broadly accepted by the mining industry and is being used to test wastes that would be disposed of in other regions.

#### **4.4.2.1 State of Nevada Meteoric Water Mobility Procedure**

The State of Nevada uses a single-pass column leach test termed the Meteoric Water Mobility Procedure (MWMP) to determine the potential for waste rock, spent ore, and tailings to release certain constituents to the environment. The test is required by guidance documents issued by the Division of Environmental Protection (NV DEP, 1990; 1996). The procedure is

provided in NV DEP (1996) and available (as of February 1999) on the internet ([www.enviromine.com/ard/Acid-Base%20Accounting/metal\\_leaching.htm](http://www.enviromine.com/ard/Acid-Base%20Accounting/metal_leaching.htm)).

The MWMP test uses 5 kg of material crushed to particle sizes smaller than 5 cm which is loaded into an extraction column. A volume of extraction fluid equal to the dry weight of the sample (milliliters of fluid equal to grams of sample) is passed through the sample in a 24 hour period. Although the procedure states that the pH of the extraction fluid should “reflect the pH of precipitation in the geographic region in which the mine rock is being evaluated,” the procedure uses Type II reagent grade water (distilled or deionized as produced by Method 1080 in APHA et al., 1992) as the extraction fluid. The pH values of the initial leachate and homogenized leachate at the end of testing are recorded. The homogenized leachate is filtered and analyzed for dissolved constituents.

#### **4.4.3 Other Leaching Procedures**

Leach test procedures also have been developed by the Province of British Columbia, the U.S. Army Corps of Engineers, and the American Society for Testing and Materials (ASTM). These tests are not widely used by the American mining industry.

##### **4.4.3.1 British Columbia Procedures**

The British Columbia Special Waste Extraction Procedure (SWEP) is a single batch extraction that uses an acetic acid lixiviant, a 16:1 liquid:solid mass ratio, and an extraction time of 24 hours. According to Mills (1998f), for mine wastes in British Columbia, it is standard practice to use distilled water or 0.1 N hydrochloric acid as the extract fluid, a liquid:solid mass ratio of 3:1, and an extraction time of 24 hours.

##### **4.4.3.2 U.S. Army Corps of Engineers Procedures**

The U.S. Army Corps of Engineers developed a procedure to conduct sequential batch leaching tests (SBLT) of dredged materials (Brannon et al., 1994). This procedure, which determines changes in the equilibrium distribution of a contaminant between solid material and an aqueous phase, can be used to investigate the quality of water that might be expected to occur during episodic flushing of mining wastes (for example, during wet winters and dry summers). The SBLT procedure uses a liquid:solid weight ratio of 4:1 and a 24-hour leaching time for each step. Samples are placed into a tumbler and tumbled using deoxygenated water as the leaching medium. The leachate is separated by centrifuge, filtered, preserved with nitric acid, and analyzed for electrical conductivity and metals. A minimum of four sequential cycles are recommended. The procedure provides a conservative estimate of leachate concentrations under conditions of anaerobic leaching of freshwater sediments (Brannon et al., 1994). The SBLT procedure could be applied to analysis of tailings and other fine-grained materials, such as borrow soils used for growth media and covers. However, the procedure does not define the size fractions that should be tested and its applicability to tests of coarse waste rock has not been demonstrated.

Myers and Brannon (1988) and Myers et al. (1991) describe a procedure developed by the U.S. Army Corps of Engineers for column leach testing of dredged freshwater sediments. These tests are recommended to confirm the results of sequential batch leaching tests and can be used if the potential for contamination is high. The Myers et al. (1991) procedure uses an improved column design that increases the number of pore volumes that can be eluted in a given period of time by using a decreased column length and increased column diameter (producing pore water velocities of approximately  $10^{-5}$  cm/sec). The test, which uses kilogram samples, is conducted using deoxygenated water as the leaching medium.

Graded serial batch tests are described by Houle and Long (1978; 1980). In these tests, solid waste is mixed with an extraction fluid in a liquid:solid ratio of 2:1 and shaken intermittently for 24 hours. The sample is filtered and the leachate analyzed, with residual solid material returned to the extraction vessel for subsequent leaching. The liquid:solid ratio is doubled for each succeeding extraction (i.e., 4:1, 8:1, 16:1, etc.), with a total of seven leach cycles recommended for each sample. The extraction fluid can be reagent water or any site-specific fluid, thus permitting a determination of the constituents that can be removed from or adsorbed by the solid waste.

#### **4.4.3.3 ASTM Procedures**

The American Society for Testing and Materials provides methodologies for conducting shake flask extractions (ASTM Method D3987) and sequential batch extractions of solid wastes (ASTM Methods D4793 and D5284) (ASTM, 1996). The tests use liquid:solid mass ratios of 20:1 and extraction times of 18 hours. In the sequential batch tests, 10 leachate samples are produced from a single solid waste sample. Methods D3987 and D4793 use water for the extraction fluid whereas method D5284 uses an acidic extraction fluid with a pH similar to that of the average regional precipitation in the disposal area.

#### **4.4.4 State Recommendations**

The states comprising EPA Region 10 presently have not promulgated formal guidelines that specify use of a particular leaching procedure. The State of Nevada recommends use of the Nevada Meteoric Water Mobility Procedure to test representative samples of waste rock, spent ore and tailings for their potential to release contaminants (NV DEP, 1996). The State of New Mexico (NMED, 1996) recommends use of EPA method 1312 (SPLP test) to test samples for the potential to release contaminants. Applicants should check with state agencies to determine whether they have preferences that may not be codified.

#### **4.4.5 Comparison of Leaching Procedures**

Batch leach tests vary significantly in their ability to extract metals from solid materials depending on the type of extraction fluid employed. EPA Method 1312 (SPLP) is best suited to mining wastes because it utilizes strong acids similar to those that would be generated under oxidizing conditions. However, the SPLP test uses a combination of sulfuric and nitric acids as the extraction fluid, which precludes determination of sulfate and nitrate concentrations in test leachates. Because these constituents may be of interest (sulfates as oxidation products of

sulfides or hydrolysis products of acid-sulfate minerals; nitrates as blasting residue), it may be practical to modify the procedure to substitute a strong acid such as hydrochloric acid, which has similar, albeit less oxidizing, qualities, as the extraction fluid. The SPLP test also can be modified to be more aggressive by decreasing the pH of the extraction fluid. The SPLP test is run under conditions of high fluid to solid ratio (20:1) and short duration (18 hours), which limits the extent to which biological oxidation will breakdown reactive sulfide minerals.

Sequential leach tests provide data regarding the rate at which constituents could be released to the environment. In particular, these tests can show whether the concentrations of metals in a leachate exhibit temporal trends. However, extrapolating the results of sequential leach tests to the expected conditions of waste disposal may not be straightforward since most tests are conducted on material that may have significantly different reaction kinetics than the actual waste (due to particle size) and because extraction durations and the amount of time between extractions do not replicate either natural wet-dry cycles or conditions of atmospheric oxidation.

Many leaching tests use reagent-grade water as the extraction fluid, which may not simulate the expected natural conditions, for example, where acidification occurs at depth in a waste pile. To more closely approximate leaching in regions where rainfall is acidic, reagent water can be acidified using strong acids to pH values typical of the regional precipitation. A more acidic extraction fluid makes leaching tests chemically more aggressive; consequently, their results provide a more conservative estimate of the potential impacts of mining materials on water quality.

A recent study by Doyle et al. (1998) leached samples of mining wastes using batch (SPLP) and continuous column procedures. They found that batch tests tended to predict higher metals leachability than the column tests (but not always), suggesting that they typically provide a more conservative estimate of environmental behavior. However, the study did not indicate which test methods better represented actual field conditions.

## **5.0 ANALYSIS OF FATE AND TRANSPORT**

Analyzing chemical fate and transport at mine sites is a complex task due to the interactions between the hydrologic cycle, pollutant cycle, and sedimentation (watershed) cycle (Bonazountas, 1983). Consequently, fate modeling includes processes that occur on the land surface (soil, atmosphere and water), the unsaturated zone, and the saturated zone (Bonazountas, 1983). Anderson and Woessner (1992) describe a modeling protocol for ground water systems that can be extended and applied to mine sites. It includes establishing the purpose of the model, developing a conceptual model, selecting governing equations and an appropriate computer code, and designing, verifying and calibrating a numerical model.

### **5.1 Developing a Conceptual Model**

A conceptual model is a pictorial representation of a complex system, frequently in the form of a block diagram or cross-section (Anderson and Woessner, 1992). The conceptual

model simplifies a complex field problem and makes it more amenable to modeling. In particular, it helps to determine the dimensions of the numerical model and the design of an appropriate grid. An example of a conceptual physical ground water model taken from Anderson and Woessner (1992) is shown in Figure C-1. A conceptual physicochemical model of metal transport in a river, taken from Schnoor (1996), is shown in Figure C-2.

Four information components are needed to develop a conceptual site model (Bedient et al., 1994). Geology provides the physical framework within which subsurface fluids collect and flow and an understanding of the characteristics of the materials and solid wastes that must be handled. Hydrology describes the movement of fluids across the surface and through the physical framework (subsurface). Chemistry defines the nature of the chemical constituents transported by the surface and subsurface flow systems, including aspects of biochemistry as they apply to fluid chemistry. Climate provides data to describe interactions between precipitation, evaporation, surface flow, subsurface flow, and infiltration.

The amount of data required to develop a mine-site conceptual model of fate and transport are considerable (Schnoor, 1996; Hemond and Fechner, 1994; U.S. EPA, 1989). The mine plan provides information about the locations, character, and volumes of materials and wastes, surface and subsurface disturbances, ground water withdrawals, surface water diversions, and outfall locations and discharges. The solids balance describes the amount and character of material that will be excavated, processed, and disposed. The water balance characterizes the effects of climatic variations, drawdown, surface water diversion, and waste water discharge.

#### Surface water

hydrology provides information regarding discharges and their seasonal variation, surface water chemistry, and storm runoff. Ground water hydrology describes flow rates (flux), hydrologic gradients, ground water volumes, ground water chemistry, and flow paths. Geology provides data on vertical stratigraphy (including aquitards), lateral changes in stratigraphic relations, the locations and density of faults and fractures, and mineralogy. Aquifer characteristics include physical aspects such as hydraulic conductivity, porosity, and fracture and matrix flow and chemical aspects including adsorptive or neutralizing components and biogeochemical processes. Contaminant characteristics describe the chemistry, density, discharge, volume, and chemical and physical stability of solid and liquid wastes and materials.

## 5.2 Mathematical Models

Mathematical models that couple physical flow and chemical mass balance equations are used to simulate the flow and transport of contaminants through the environment. Because models used for predictive purposes are only as good as the data input to them, high quality, site-specific data are required to produce confident and realistic model predictions.

### 5.2.1 Categories of Mathematical Models

Mathematical models can be grouped into three general categories (Knox et al., 1993). *Analytical models* solve governing equations using simplifying assumptions. They are generally one- or two-dimensional models that assume steady-state flow. *Stochastic models* incorporate uncertainty by using mean values coupled with a measure of variance. *Numerical models*, which

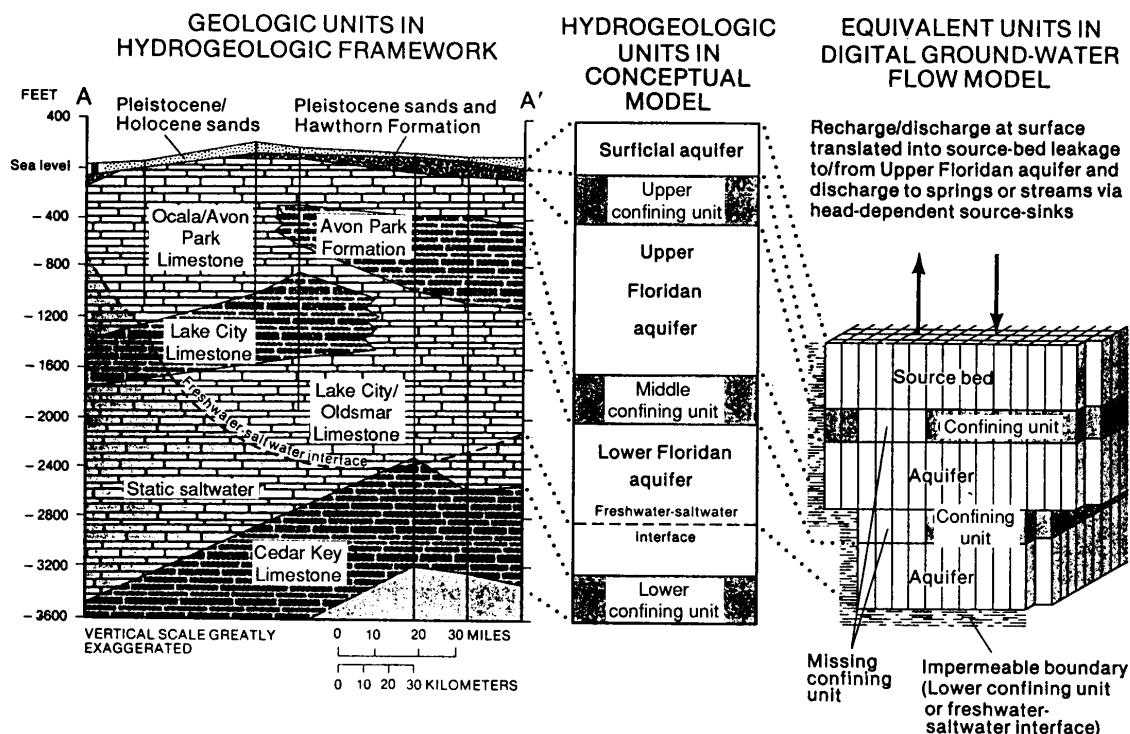


Figure C-1. Conceptual physical model of ground water flow from Anderson and Woessner (1992).

are the most commonly used model form, are computed solutions to coupled partial differential equations of flow and mass balance equations of contaminant fate. Numerical models are solved in one-, two-, or three-dimensions using either finite element, finite difference, or method of characteristics techniques. Detailed discussions of each of these methods can be found in Knox et al. (1993) and Bedient et al. (1994).



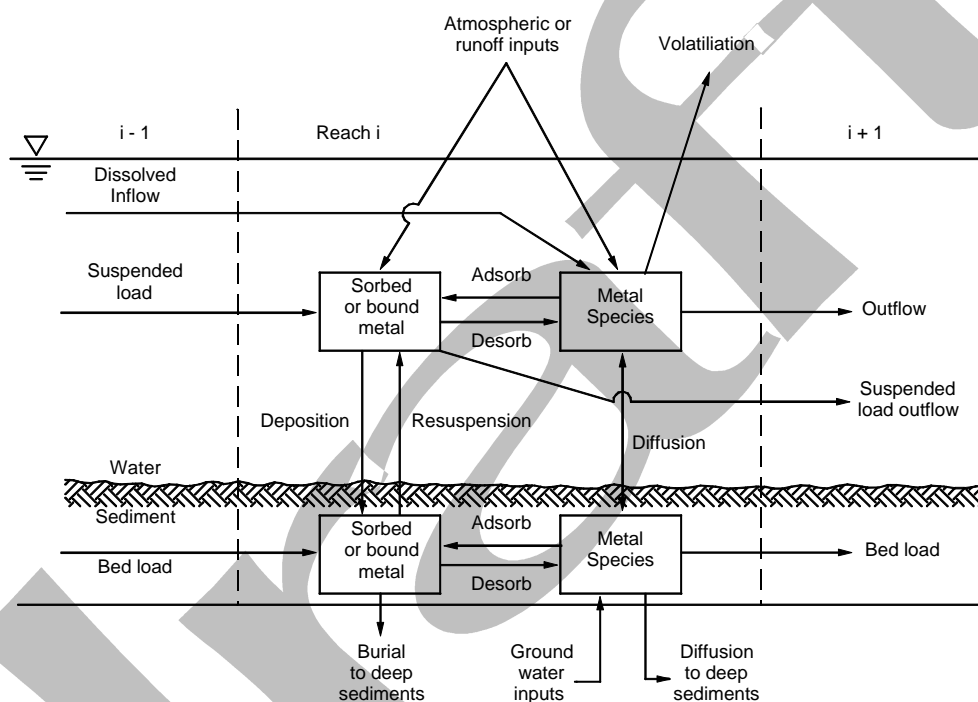


Figure C-2. Conceptual physicochemical model of metal transport in a river from Schnoor (1996).

### 5.2.2 Chemical Equilibrium Models

Numerous physical, chemical, and biological processes occurring in surface and subsurface environments can affect the transport and fate of contaminants. These can be divided into abiotic and biotic processes (Keely, 1989a). Abiotic processes are physical and chemical interactions that cause contaminants to move at a rate different from that of surface or ground water. They include hydrolysis, sorption, cosolvation, immiscibility, ionization, radionuclide decay, complexation, volatilization, photodegradation, precipitation, dissolution, and reduction-oxidation (Johnson et al., 1989; Schnoor, 1996). Biotic processes are microbially mediated transformations or adsorption of contaminants. They include biodegradation and bioaccumulation. Other physical processes that may affect contaminant concentrations include hydrodynamic dispersion, molecular diffusion, and density stratification (Knox et al., 1993).

Chemical equilibrium models calculate changes in chemical concentrations assuming equilibrium. Aqueous models of trace metal concentrations compute chemical species by accounting for aqueous-phase complexation (e.g., by naturally occurring humic acids), surface complexation (e.g., by ion-exchange on the surfaces of clays), adsorption and sedimentation by particles (e.g., lead adsorbed on the surface of ferric hydroxide), mineral precipitation (e.g., ferric hydroxide), mineral dissolution (e.g., calcite dissolution by acid), aggregation/flocculation (e.g., the formation of colloidal suspensions by electrostatic processes), redox reactions that affect solubility (e.g.,  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$ ), and adsorption by soil particles (Johnson et al., 1989; Schnoor, 1996). Summary descriptions of three chemical equilibrium models, MacqQL, MINEQL+, and MINTEQA2, are given in Schnoor (1996).

### 5.2.3 Physical Flow and Transport Models

Flow and solute (mass) transport models are available for surface water, ground water (saturated zone), and the vadose zone (unsaturated zone). They typically are used in conjunction with one of the equilibrium chemical models described above. The mathematical development of the governing flow and transport equations used in many of these models is given in Schnoor (1996).

Models commonly used to compute river water quality include QUAL2EU, NONEQUI, and WASP (summary descriptions are given in Schnoor, 1996 and are available via the internet on sites for the U.S. EPA's Robert S. Kerr Environmental Research Lab and Center for Exposure Assessment Modeling). QUAL2EU is a steady-state model for pollutants in branching streams and well-mixed lakes that incorporates uncertainty analysis into the model results.

Keely (1989b) points out that many ground water models are inappropriate for use in areas where subsurface flow is controlled by fractures or karst features. Consequently, the choice of models determines whether realistic model predictions can be computed for these areas. Bedient et al. (1994) provide summary model descriptions and a listing of modeled processes for a variety of unsaturated and saturated flow and solute transport models. Included are 6 vadose-zone flow models, 11 vadose-zone solute transport models, 12 saturated zone flow models, and 9 saturated zone solute transport models. Additional model descriptions are available via the internet from the U.S. EPA's Robert S. Kerr Environmental Research Lab. Among the more

widely used saturated zone models are MODFLOW, a three-dimensional finite difference model, and USGS-MOC, a two-dimensional finite difference and methods of characteristics model for ground water flow and solute transport. Anderson and Woessner (1992) describe three conceptual models that can be used to approximate flow through a fractured system for input to models based on saturated or unsaturated flow. Each of these conceptual models uses assumptions that oversimplify flow through the fractured system.

## **6.0 SAMPLING PROGRAMS**

The environmental sampling process should follow a sequence of steps to ensure that collected samples are representative and adequate (Triegel, 1988). It is important to first identify the goals of the sampling program and the levels of confidence required. The number of required samples then can be determined by characterizing the sources of variability (e.g., sample heterogeneity). Using these data, the sample program can be designed. The design should consider the types of analyses that will be conducted on the samples and include the number and distribution of samples and their manner of collection. The following sections specifically address geochemical testing programs.

### **6.1 Objectives of a Geochemical Sampling Program**

Establishing a reliable geochemical testing program is a difficult, but critical, aspect of mine site development. By indicating whether control technologies or alternative disposal methods should be added to the existing mine plan, a robust program that uses representative samples can diminish, perhaps eliminate, the costs of contamination mitigation and control that would be encumbered should environmental problems arise in the future (Robertson and Broughton, 1992).

The geologic history and nature of mineralization observed at a mine site is unique to that particular location. As a result, geochemical sampling programs will differ from site to site. Nevertheless, all sampling programs should strive to capture the range of variability that occurs, provide an accurate statistical representation of the materials present, and objectively test the feasibility of the disposal methods described by the proposed mine plan. A geochemical sampling program should consider several factors that could affect the chemical or physical character of samples and, consequently, impact test results. Included are the method of sample collection, the length of time that a sample will be (or has been) stored prior to analysis, and the environment in which samples are (or were) stored (U.S. EPA, 1994).

For proposed mines, sampling and testing programs use fresh samples to predict the potential for acid generating conditions to develop or metals to leach from materials and wastes (Robertson and Broughton, 1992). A sampling program should be related directly to a mine plan that outlines the area to be mined, the locations of pit walls and benches or underground workings, the locations and amounts of ore and waste rock that will be excavated, and the approximate timing of excavation and final placement of the materials (BC AMD Task Force, 1989). The latter is especially important for determining the potential for contaminant release from waste rock dumps because these features can vary in particle size, particle mineralogy, and

chemical composition over short distances. The sampling program also should include materials produced during bench-scale or pilot-scale processing tests conducted on samples that encompass the range of materials that will be processed over the life of the operation. Geochemical and mineralogical variability can be evaluated using three-dimensional geostatistical techniques similar to those used to describe the ore body (Robertson and Broughton, 1992).

Sampling and testing programs at existing or abandoned mines should address questions regarding the quantity of acid products stored in the materials and wastes and how contamination emanating from them is likely to change in the future (Robertson and Broughton, 1992). For studies of existing waste rock dumps, spent ore heaps, or tailings piles, a sampling program must establish the physical, mineralogical, and chemical variability of the materials and wastes (see Nash et al., 1998).

## **6.2 Sample Representativeness**

Samples used in geochemical tests should be representative of the materials that will be mined and processed. According to Smith et al. (1988), representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or a process or environmental condition. Indeed, the major source of uncertainty in a sampling and testing program lies in the samples themselves. In particular, the question of how accurately a sample represents a larger volume of material can only be addressed by establishing the variation inherent in the geochemical rock unit by taking multiple samples and examining their frequency distribution (BC AMD Task Force, 1990).

### **6.2.1 Proposed Mine Sites**

Tests to determine physical and geochemical variability should be conducted initially on each lithologic unit that will be excavated, exposed or otherwise disrupted in a mine site area. They should use as their basis the mineralogical zonation observed within the ore body and, if possible, the mineralogical distinction that separates ore material from waste rock. The results of initial tests can be used to define units with similar geochemical and leachate production attributes (i.e., geochemical rock units; Brodie et al., 1991). In some cases, test results will require that a heterogeneous lithologic unit be divided into two or more geochemical rock units, whereas in other cases, two or more homogeneous lithologic units may be grouped together. Each geochemical rock unit should be tested further to define the range of its geochemical characteristics. In essence, a sampling program uses an iterative process to assess variability and it must be designed to be sufficiently flexible to respond to changes in the mining plan (Robertson and Broughton, 1992).

Geochemical test samples should be collected from each geochemical rock unit over the full vertical and areal extent of the mine site or area of interest. Geographical representativeness can be depicted using maps and cross-sections. The number of samples that should be tested depends on the volume and variability of the rock unit in question. In general, sample requirements increase with chemical and mineralogical heterogeneity. As a general guide for acid-base accounting tests, the BC AMD Task Force (1989) recommended a minimum number of samples appropriate for a rock unit with a given mass (Figure C-3). This approach can lead to

extensive sampling requirements for large facilities and result in inordinately high sampling costs.

As an alternative, Runnells et al. (1997) suggested that the number of required samples should reflect the heterogeneity of the materials within the facility. The appropriate number of samples is obtained when statistical variability in sample results is within acceptable limits. Using this approach, the number of samples needed to characterize a facility will vary from one facility to another because each facility is unique. The Runnells et al. (1997) method can be applied easily to existing facilities, but may be difficult to apply to materials that would be disposed of in proposed facilities. Nevertheless, sampling programs that use a fixed-frequency sampling approach should be designed to ensure that sample variability can be described with statistical validity (e.g., BC AMD Task Force, 1990).

Geologic materials, which are composed of one or more minerals, are by definition composite materials. For the purposes of geochemical testing, sample sizes should be large enough to smooth the effects of small-scale heterogeneity, but small enough to reveal the variations present in the rock unit of interest. The effects of composite sample size on the distribution of net neutralization potential values obtained from a highly variable rock mass are described by Robertson and Broughton (1992). For waste rock and overburden materials, samples are commonly lengths of drill core or drill cuttings. Robertson and Broughton (1992) suggest restricting drill core lengths to less than 0.5 meters for acid-base accounting tests to ensure that the chemical behavior of a waste rock pile can be evaluated on small and large scales.

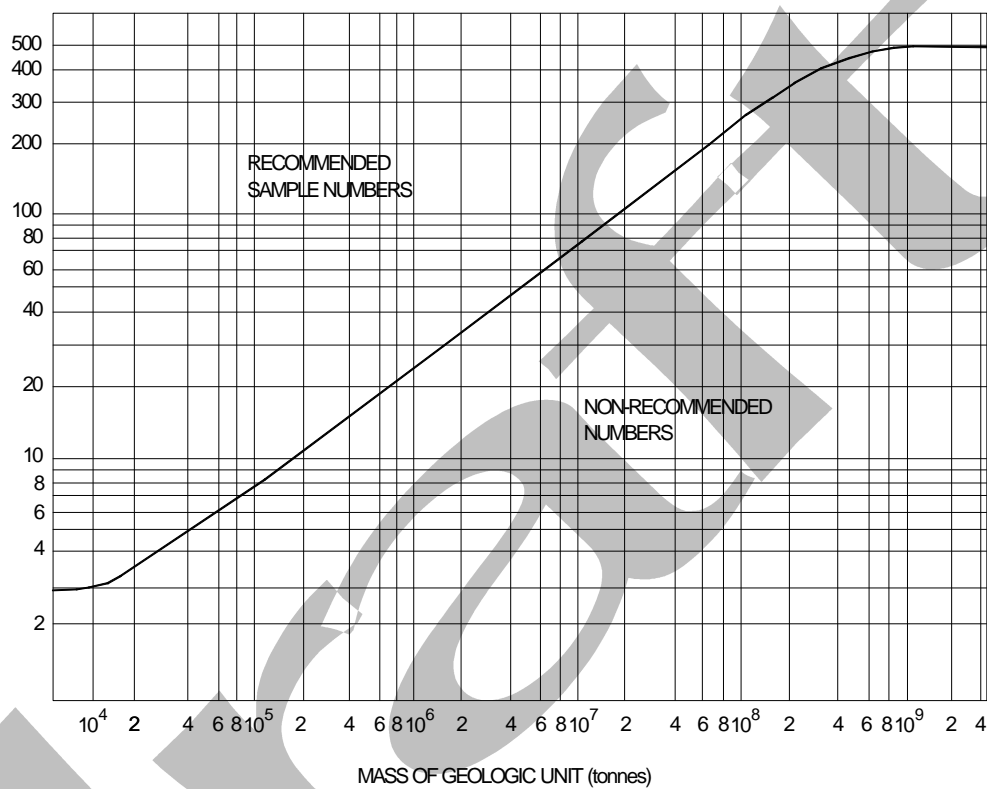


Figure C-3. Recommended minimum number of samples as a function of rock mass (BC AMD Task Force, 1989).

## 6.2.2 Existing or Abandoned Mine Sites

Existing or abandoned mine sites can pose special problems for geochemical test sampling because the history of the mine and the detailed composition of materials and wastes may be unknown or unrecorded. Changes to processing methods and efficiency that may have occurred during active production or time gaps when mining did not occur can produce chemical and physical heterogeneity within piles of materials that are not evident from their exposed surfaces. Consequently, sampling programs designed for existing or abandoned mine sites should determine the variability of all materials disposed of or exposed on the surface (see discussion of Runnells et al. 1997 in Section 6.2.1 and Nash et al., 1998). For pit walls, this will require collecting samples vertically and laterally across the exposed rock faces. For waste rock dumps, spent ore heaps, and tailings impoundments, it will require collecting samples laterally and vertically throughout the deposit (typically by drilling) (Nash et al., 1998). Data gathered from these samples can be used to construct a three-dimensional image of the volume and chemical and physical character of the waste materials. As described in the previous section, the number of samples required by the program depends on the volume and variability of the materials in question, but generally increases with chemical, mineralogical, and physical heterogeneity.

## 6.3 Quality Control and Quality Assurance

A recent report by Downing and Mills (1998) describes the application of quality assurance and quality control procedures as they apply to acid rock drainage studies. QA/QC guidance and procedures prepared by EPA are available in Adobe format on the EPA Region 10 QA website ([www.epa.gov/r10earth/offices/oea/qaindex.htm](http://www.epa.gov/r10earth/offices/oea/qaindex.htm)). New guidance for the preparation of QAPP documents is in review and is scheduled for issue in early 1999.

### 6.3.1 Quality Control

Taylor (1988) defines quality control as the application of good lab practices, good measurement practices, and standard procedures for sampling. The latter should include specifications for chain-of custody, storage and preservation, stabilization methods, labeling, and sample containers.

Physical and geochemical tests conducted using approved methods (EPA or otherwise) will produce analytical results with accuracy and precision sufficient for all likely applications, providing that methods are chosen for their ability to meet the data quality objectives described in the next section. In this regard, it is important for applicants to select analytical methods that have the necessary detection limits. Applicants should periodically submit replicate samples for testing and analysis to confirm laboratory assessments of analytical performance.

### 6.3.2 Quality Assurance

Quality assurance is the process of monitoring for adherence to quality control protocols (Taylor, 1988). Smith et al. (1988) list five data quality objectives of a quality assurance project plan (QAPP): precision, bias, representativeness, completeness, and comparability (cf. U.S. EPA,

1980; 1998a; 1998b). Precision leads to a measurement of variance (e.g., standard deviation) and is the mutual agreement among individual measurements under prescribed similar conditions. Bias refers to the degree to which a measurement reflects an accepted true or reference value, commonly expressed as a percentage. Representativeness, as described above, expresses the degree to which data accurately represent a characteristic of a population. Completeness is a measure of the amount of valid data compared to the amount expected to be obtained under normal conditions. Comparability is a measure of confidence that one data set can be compared to another.

A QAPP will ensure that procedures are established prior to the beginning of sample collection and will help to balance the costs of implementing a quality-assured program against the liabilities of a poorly designed and executed sampling program.

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